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# Zinc Coordination Polymers Containing Isomeric Forms of p-(Thiazolyl)benzoic Acid: Blue-Emitting Materials with a Solvatochromic Response to Water

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## Abstract

© 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim Two coordination polymers of assorted dimensionality (1D, 2D) have been prepared, namely [Zn 3 (L 2Th ) 4 (OH) 2 ·2(HL 2Th )] ∞ (1) and [Zn(L 5Th )(OAc)] ∞ (2), starting from Zn II salts and the isomeric forms of the organic linker p-(thiazolyl)benzoic acid: p-(2-thiazolyl)benzoic acid (HL 2Th ) and p-(5-thiazolyl)benzoic acid (HL 5Th ). The isomers have been prepared ad hoc, following straightforward Pd-catalyzed C–C coupling reaction protocols. In 1, the deprotonated ligand is coordinated through its carboxylate group only, with dangling thiazole groups. The –COO – units are bridging adjacent metal centers, thus creating a 1D chain. The Zn 3 cluster is made of one six-coordinate (O h ) and two four-coordinate (T d ) Zn II ions; triple-bridging μ 3 -OH groups are balancing the overall positive charge. The structure of 2 is instead made of Zn 2 (carboxylate) 4 “paddle-wheel” dimers as the constituting inorganic node. The octahedral metal coordination sphere includes two μ-(κ-COO) benzoate spacers, two μ-(κ-COO) acetate ions, the thiazole N atoms coming from adjacent building blocks, and a weak Zn···Zn axial interaction. The resulting final assembly is two-dimensional (2D), where p-(5-thiazolyl)benzoate adopts a genuine μ-[κ(COO):κ(N)] bridging coordination mode. The luminescent properties of both polymers have been analyzed in the solid state; they feature ligand-centered emissions at λ = 434 nm (1) and λ = 427 nm (2). These electronic transitions fall in the visible region, giving the samples a characteristic blue color under an ordinary UV lamp (excitation at λ = 254 nm). The theoretical analysis of the electronic features of the ligands and related molecular orbitals reveals that the observed transitions are mainly of π→π* nature, involving π orbitals delocalized on both aromatic cycles. A significant (reversible) blueshift of the emission maximum of ca. 60 nm, from the visible to the UV region, has been observed for 1 when suspended in water.

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## Keywords

Coordination polymers, Luminescence, Solvatochromism, Thiazole, Zinc

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